

**AMENDMENTS TO THE DRAWINGS**

Add Figs. 5 and 6 submitted herewith. Fig. 5 is an illustration of a boron phosphide crystal layer containing stacking faults and twins with twin boundaries. Fig. 6 is a microphotograph showing stacking faults and twins in a BP layer grown on a SiC support. These drawings are submitted pursuant to 37 C.F.R. § 1.83 and the Examiner's request for drawings which illustrate the stacking fault and twin features of claims 7 and 8. No new matter has been added.

Attachment: New Sheets (Figs. 5 and 6)  
Replacement Sheets (Figs. 1-6 including new drawings Figs. 5 and 6)

**REMARKS**

Claims 1, 2, 11-15 and 18 are rejected; claims 16 and 17 are allowed; and claims 3-10 are objected to as being allowable if rewritten in independent form.

Pursuant to 37 C.F.R. § 1.83(a) and the Examiner's request, the specification has been amended to add Figs. 5 and 6 showing the features of a "stacking fault" and a "twin with a twin boundary" as claimed in claim 7. No new matter has been added, because Figs. 5 and 6 simply illustrate structural features of the boron phosphide crystal layer as described and claimed in the specification as originally filed. The specification bridging pages 6-7 has been amended to include a description of new Figs. 5 and 6 under the heading "BRIEF DESCRIPTION OF THE DRAWINGS".

Fig. 6 (microphotograph) is taken from the paper by T. Udagawa et al., "High-resolution TEM characterization of MOVPE-grown (1 1 1)-BP layer on hexagonal 6H (0 0 0 1)-SiC", Applied Surface Science 244 (2005), pp. 285-288, copy attached. Takashi Udagawa is the sole inventor of the invention described and claimed in the above-identified application.

Claims 1 and 11 have been amended to incorporate therein the recitation of claim 2. Claims 2, 4, 6, 8 and 10 have been canceled. Claim 14 has been amended to incorporate therein the recitation of claim 15. Claim 15 has been canceled.

In response to the rejection under 35 U.S.C. § 112, second paragraph, the language of claim 2 as incorporated into claims 1 and 11 has been amended to replace "non-crystalline layer" with --an amorphous layer-- as described in the specification. Claim 18 has been similarly amended.

Withdrawal of the foregoing rejection under 35 U.S.C. § 112, second paragraph, is respectfully requested.

Claims 1 and 11-14 were rejected under 35 U.S.C. § 102(b) as being anticipated by U.S. Patent 5,076,860 to Ohba et al. The Examiner cited several figures of Ohba et al., including Fig. 15, as meeting the terms of the rejected claims.

In response, claims 1 and 11 have been amended to incorporate therein the recitation of claim 2 and claim 14 has been amended to incorporate the recitation of claim 15, to thereby obviate the foregoing rejection. Claims 2 and 15 were not rejected over prior art. Claim 2 as incorporated into claims 1 and 11 recites that the Group-III nitrides semiconductor device further comprises an amorphous layer containing boron and phosphorous provided between the Group-III nitride semiconductor crystal layer and boron phosphide crystal layer. Claim 15 as incorporated into claim 14 recites the light-emitting device further comprises a phosphorous layer containing boron and phosphorous provided between at least one of (i) the lower clad layer and the boron phosphide crystal layer of the first conduction type and (ii) the upper clad layer and the boron phosphide crystal layer of the second conduction type. The features of claims 2 and 15 are not disclosed by the cited prior art.

Withdrawal of all rejections and allowance of claims 1, 3, 5, 7, 9, 11-14 and 16-18 is earnestly solicited.

In the event that the Examiner believes that it may be helpful to advance the prosecution of this application, the Examiner is invited to contact the undersigned at the local Washington, D.C. telephone number indicated below.

AMENDMENT UNDER 37 C.F.R. § 1.111  
U.S. Application No. 10/689,024

Q72568

The USPTO is directed and authorized to charge all required fees, except for the Issue Fee and the Publication Fee, to Deposit Account No. 19-4880. Please also credit any overpayments to said Deposit Account.

Respectfully submitted,



---

Abraham J. Rosner  
Registration No. 33,276

SUGHRUE MION, PLLC  
Telephone: (202) 293-7060  
Facsimile: (202) 293-7860

WASHINGTON OFFICE

**23373**

CUSTOMER NUMBER

Date: November 14, 2005



## High-resolution TEM characterization of MOVPE-grown (1 1 1)-BP layer on hexagonal 6H (0 0 0 1)-SiC

T. Udagawa<sup>a,\*</sup>, M. Odawara<sup>b</sup>, G. Shimaoka<sup>c</sup>

<sup>a</sup>Corporate Technical Department (Chichibu), Technology Headquarters, Showa Denko K.K.,  
1505-Shimokagemori, Chichibu, Saitama 369-1871, Japan

<sup>b</sup>Electronics Materials Division, Electronics Sector, Showa Denko K.K., 1505-Shimokagemori, Chichibu, Saitama 369-1871, Japan

<sup>c</sup>Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Hamamatsu, Shizuoka 432-8011, Japan

Received 28 May 2004; accepted 22 October 2004

Available online 9 January 2005

### Abstract

A BP layer was grown on the (0 0 0 1)-surface of 6H-type hexagonal SiC substrate by atmospheric-pressure metalorganic VPE, and crystallographic feature of the resultant BP/SiC hetero-structure was evaluated by transmission electron microscopy (TEM) and transmission electron diffraction (TED). Analysis of the TED patterns from the hetero-structure gave the following epitaxial relationship: (0 0 0 1), <a-axes>-SiC // (1 1 1), <1 1 0>-BP. Extra diffraction spots in the TED pattern indicated the presence of {1 1 1}-twins in the (1 1 1)-BP layer. High-resolution TEM observation also revealed the presence of random texture which involved irregular configuration of atomic planes in the (1 1 1)-BP layer at the hetero-interface with the (0 0 0 1)-SiC. The MOCVD-grown (1 1 1)-BP layer was deduced to develop on the (0 0 0 1)-SiC, accompanying the formation of the (1 1 1)-twins and of the random texture at the interface with the (0 0 0 1)-SiC.

© 2004 Published by Elsevier B.V.

PACS: 61.16.Bg; 61.72.Nn; 68.55.-a

Keywords: Characterization; Metalorganic chemical vapor deposition; III–V Semiconductors

### 1. Introduction

Boron phosphide (BP) attracts attention as a wide band-gap and refractive III–V compound semiconductors which are applicable to form semiconductor hetero-structures [1,2]. Up to now, BP layers have

been prepared by various vapor-phase epitaxy (VPE) procedures, such as halide-VPE and metalorganic VPE (MOVPE), to form hetero-junctions with diamond structure Si [3,4] and wurtzite structure GaN [5,6]. Boron phosphide layers grown by halide- and hydride-VPE methods were also used to form the hetero-junction with hexagonal structure SiC [7].

According to the previous study on the VPE growth of BP layer [7], the epitaxial growth of BP layer was predicted to be promoted by coalescence of BP

\* Corresponding author. Tel.: +81 494 23 6117;  
fax: +81 494 25 0830.

E-mail address: [takasi\\_udagawa@sdk.co.jp](mailto:takasi_udagawa@sdk.co.jp) (T. Udagawa).

crystallites with formation of stacking faults [7]. In contrast to this, growth manner of BP grown by MOVPE using an organic boron compound as a boron source has not been reported so far.

In this report, BP layer is grown on hexagonal 6H-type SiC by MOVPE technique alternative to the halide- and hydride-VPE procedures, and hetero-epitaxial growth feature of the BP on the 6H-SiC is investigated with relation to the formation of crystal-line imperfections.

## 2. Experimental procedure

An undoped BP layer was grown at 850–950 °C on the (0 0 0 1)-surface of 6H-type hexagonal SiC substrate by means of MOVPE procedure using triethylboran ( $(\text{C}_2\text{H}_5)_3\text{B}$ ) (Rohm and Haas electronic materials LLC, USA) and phosphine ( $\text{PH}_3$ ) for boron (B) and phosphorus (P) source gases, respectively. The source gases were transported with hydrogen gas ( $\text{H}_2$ ) to a quartz-made horizontal MOVPE reactor. The growth of the BP layer was done under atmospheric pressure. In the MOVPE growth of the BP layer, concentration ratio of source gases fed into the reactor, i.e.,  $\text{PH}_3/(\text{C}_2\text{H}_5)_3\text{B}$  ratio, was kept about 600. The thickness of the grown BP layer was ranged from about 200 to 440 nm. Epitaxial relationship of the BP layer grown on the (0 0 0 1)-SiC was investigated by transmission electron diffraction (TED) using the incident beam parallel to the [2-1-10]-direction of the 6H-type hexagonal SiC. High-resolution transmission electron microscope (HRTEM) was also utilized to evaluate crystalline imperfections involved in the BP layer.

## 3. Results and discussion

Epitaxial relation between the continuous BP layers and the 6H-SiC substrates were determined by analyzing the TED patterns of the BP layers and the substrates. Fig. 1 (a) and (b) show selected-area TED patterns of the (0 0 0 1)-SiC substrate and the 440 nm thick BP layer grown on the substrate at 900 °C, respectively. In Fig. 1(c), the pattern obtained by overlapping diffraction spots from the BP layer on those from the SiC substrate is also shown. By

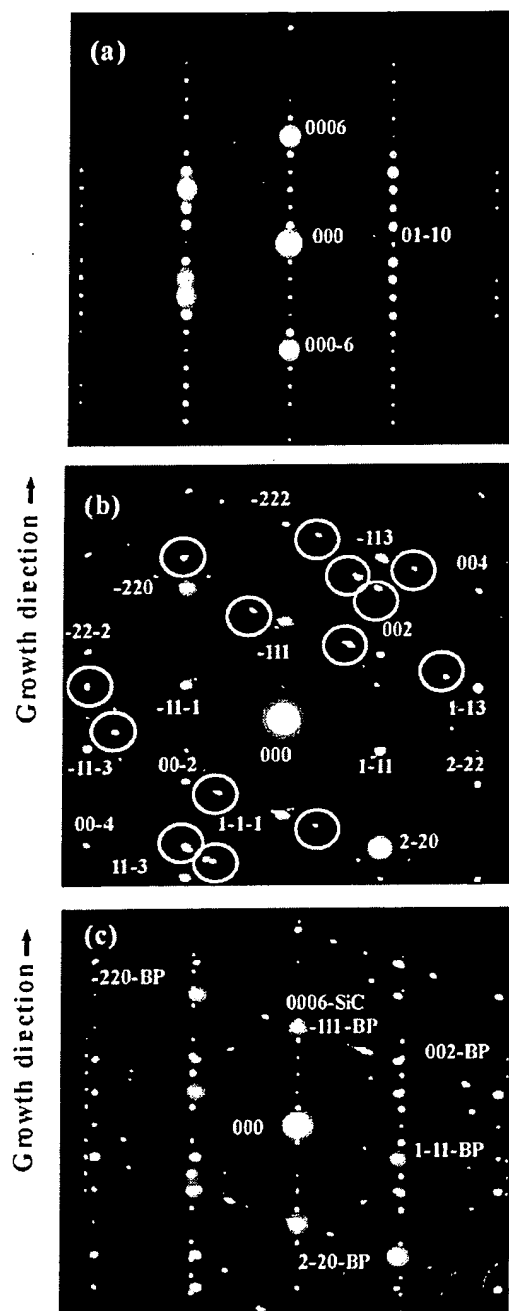


Fig. 1. Selected-area TED patterns of (a) 6H-type SiC substrate; and (b) (1 1 1)-BP layer grown on the substrate. Extra diffraction spots from {1 1 1}-twins in the (1 1 1)-BP layer are shown in open circles (○) in Fig. 1 (b). Diffraction pattern obtained by overlapping the diffractions from the SiC substrate and the (1 1 1)-BP layer is shown in (c).

The MOVPE-grown (111)-BP layer involved {111}-twins. In addition to the {111}-twins, the texture in which atomic planes of the BP layer configured randomly was formed at the hetero-interface with the (0001)-SiC. The random configuration of BP atomic planes was estimated to result from a large lattice mismatching between BP and 6H-SiC. The (111)-BP layer was therefore deduced to grow up on the (0001)-SiC, accompanying the formation of the (111)-twins and of the random texture at the interface with the SiC.

## References

- [1] T. Nishinaga, H. Ogawa, H. Watanabe, T. Arizumi, *J. Cryst. Growth* 13/14 (1972) 346.
- [2] T. Takenaka, M. Takigawa, K. Shohno, *J. Electrochem. Soc.* 125 (1978) 633.
- [3] T. Udagawa, G. Shimaoka, *J. Ceram. Process. Res.* 4 (2003) 80.
- [4] T. Udagawa, M. Odawara, T. Okano, G. Shimaoka, Abstracts of the Fourth International Workshop on Modeling in Crystal Growth, IMWCG-4, Fukuoka, Japan, November 4–7, 2003, p. 145.
- [5] T. Udagawa, M. Odawara, G. Shimaoka, *Phys. Stat. Sol. (c)* 0 (7) (2003) 2027.
- [6] T. Izumiya, A. Hatano, Y. Ohba, G. Shimaoka, Institute of Physics Conference Series No. 159, Proceedings of the International Symposium on GaAs and Related Compounds, Karuizawa, Japan, 1992, IOP Publishing Ltd., London, 1993, p. 157.
- [7] T.L. Chu, J.M. Jackson, A.H. Hyslop, S.C. Chu, *J. Appl. Phys.* 42 (1971) 420.
- [8] T. Paskova, V. Darakchieva, E. Valcheva, P.P. Paskov, B. Monemar, M. Heuken, *Phys. Stat. Sol. (b)* 240 (2) (2003) 318.
- [9] P. Hirsch, A. Howie, R. Nicholson, D.W. Pashley, M.J. Whelan, *Electron Microscopy of Thin Crystals*, Robert E. Krieger Pub. Co. Inc., Florida, 1977.

comparing the diffraction pattern of BP layer (Fig. 1(b)) with that of the SiC substrate (Fig. 1(a)), diffraction spots of  $\{111\}$ -BP were clarified to array along the growth direction of the BP layer. Since  $\{0001\}$ -diffraction spots from the SiC substrate also arrayed parallel to the growth direction, the stacking relation between the BP layer and the  $\{0001\}$ -SiC was determined as follows:  $\{0001\}$ -SiC// $\{111\}$ -BP. The obtained stacking relation agrees with that previously reported by Chu et al. [7] for a VPE-grown BP layer on a hexagonal SiC substrate. The diffraction pattern shown in Fig. 1 also shows that the  $-111$ -diffraction spot from the  $\{111\}$ -BP layer appears at almost the same position where the  $0006$ -diffraction from the  $\{0001\}$ -SiC was generated. This is owing to that the BP has lattice spacing of  $\{111\}$ -planes ( $\approx 0.262$  nm) nearly equal to that of  $\{0006\}$ -SiC ( $\approx 0.253$  nm). In addition to this, the incident electron beam parallel to  $[2-1-10]$ -direction of the SiC gave the diffraction pattern corresponding to  $\langle 110 \rangle$  projection pattern of reciprocal lattice of BP as shown in Fig. 1(b) and (c). The axial orientation between the BP layer and the SiC substrate was thus determined to be:  $\langle a\text{-axes} \rangle$ -SiC //  $\langle 110 \rangle$ -BP. The orientation relation obtained here was different to that reported for the BP layer grown by the VPE method by Chu et al. [7]:  $\langle 01-10 \rangle$ -SiC// $\langle 1-10 \rangle$ -BP. In the case of vapor-phase growth of GaN on the  $a$ -plane of sapphire, MOVPE growth procedure is also reported to give a GaN epitaxial layer with an orientation different to that of the GaN grown by hydride-VPE method [8]. Further investigation is required to investigate parameters which bring about the difference in the orientation relation between the BP and the SiC.

In the TED pattern of the  $\{111\}$ -BP layer shown in Fig. 1(b), extra diffraction spots could be seen to array along to the  $\langle 111 \rangle$ -directions of the BP layer. The extra spots were present adjacent to diffraction spots of BP, for example,  $111$  and  $1-1-1$  diffraction spots, with the distances of just one-third ( $=1/3$ ) of the lattice spacing of  $\{111\}$ -BP planes. The origin of the extra diffraction could be then attributed to twins bounded on  $\{111\}$  planes of BP as predicted by electron diffraction theory on twins in a cubic crystal [9]. The twins having the  $\{111\}$  plane as twin boundary, i.e.,  $\{111\}$ -twins, were recognized in the BP layer grown on the 6H-SiC at a temperature between 850 and

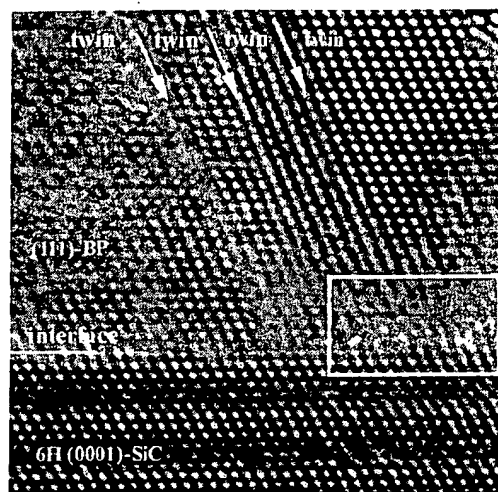


Fig. 2. High-resolution TEM image of  $\{111\}$ -twins with boundaries ( $\leftrightarrow$ ) in  $\{111\}$ -BP layer grown on the 6H-SiC substrate (magnification:  $5.3 \times 10^6$ ). A region in which atomic planes in the BP layer configures randomly is shown in the rectangular frame ( $\square$ ).

950 °C. Fig. 2 shows an HRTEM image of the  $\{111\}$ -BP layer grown at 900 °C on the  $\{0001\}$ -SiC substrate. As shown in the HRTEM image, twin boundaries which prolongs along  $\langle 111 \rangle$ -direction of the BP layer are actually observed.

A texture which involves a random configuration of atomic planes of BP was also found to present in the  $\{111\}$ -BP layer near the interface with the SiC substrate, as shown in Fig. 2. The generation of the random texture of the BP at the interface is probably related to a lattice mismatch, 47.2%, between BP with lattice constant of 0.454 nm and  $a$ -axis of the SiC ( $\approx 0.308$  nm).

#### 4. Summary

Hetero-epitaxial growth manner of the MOVPE-grown  $\{111\}$ -BP layer on the 6H-SiC was investigated. Epitaxial relationship between the BP layer and the SiC was summarized as follows:  $\{0001\}$ ,  $\langle a\text{-axes} \rangle$ -SiC// $\{111\}$ ,  $\langle 110 \rangle$ -BP. In contrast to the stacking relation of  $\{111\}$ -BP to the  $\{0001\}$ -SiC, the axial orientation of the MOVPE-grown BP layer was different to that of the  $\{111\}$ -BP layer grown by the halide- or hydride-VPE procedure.